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Potassium Binding Adjacent to Cationic Transition-Metal Fragments: Unusual Heterobimetallic Adducts of a Calix[4]arene-Based Thione Ligand

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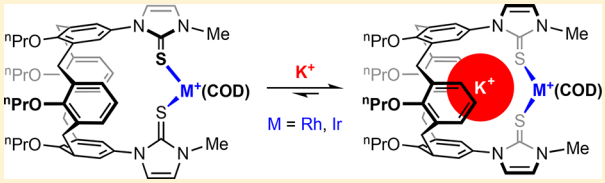
Supporting Information

ABSTRACT: The synthesis of cationic rhodium and iridium complexes of a bis(imidazole-2-thione)-functionalized calix[4]-arene ligand and their surprising capacity for potassium binding are described. In both cases, uptake of the alkali metal into the calix[4]arene cavity occurs despite adverse electrostatic interactions associated with close proximity to the transition-metal fragment [$Rh^+\cdots K^+$ = 3.715(1) Å; $Ir^+\cdots K^+$ = 3.690(1) Å]. The formation and constituent bonding of these unusual heterobimetallic adducts have been interrogated through extensive solution and solid-state characterization, examination of the host−guest chemistry of the ligand and its upper-rim unfunctionalized calix[4]arene analogue, and use of density functional theory based energy decomposition analysis.



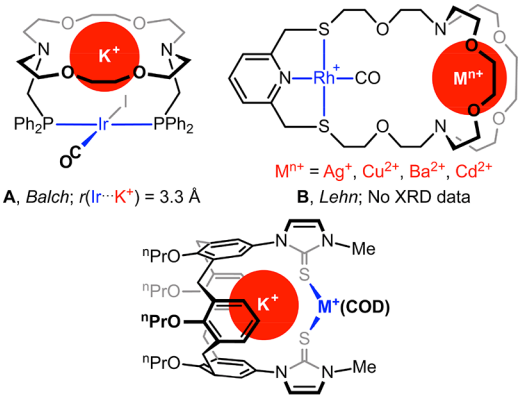
INTRODUCTION

Electrostatic forces between ions are the strongest noncovalent bonding interactions encountered in supramolecular chemistry. Correspondingly, the attraction between oppositely charged components features widely throughout the host−guest chemistry of biological and synthetic systems.[1] Conversely, repulsion between identically charged host and guest molecules is significantly destabilizing, and unsurprisingly well-defined supramolecular complexes featuring such unfavorable interactions are rare.[2,3]

As part of our ongoing work exploring the coordination chemistry of calix[4]arene-based ligands,[4] we serendipitously discovered that cationic rhodium and iridium complexes **1**, bearing bis(imidazole-2-thione)-functionalized calix[4]arene ligand **2**, show significant uptake of potassium cations (Chart 1). Although alkali-metal binding by calix[4]arenes is well documented, it is typically buttressed by the presence of alkoxide, poly(ether), or carboxyl appendages.[5] In the case of **1**, inclusion of potassium is remarkable for the adverse Coulombic repulsion associated with close proximity of a cationic metal fragment to the binding site ($M^+\cdots K^+$ = 3.7 Å, where M = Rh, Ir). Indeed, to the best of our knowledge, the nearest well-defined precedent for the host−guest chemistry observed for **1** is neutral iridium host **A** described by Balch ($Ir\cdots K^+$ = 3.3 Å; Chart 1).[6] Polycyclic rhodium systems typified by **B** and reported by Carroy and Lehn are conceptually similar, although in this case, the guest cations are held significantly more remote from the rhodium center.[3]

Herein we describe the synthesis of **1** and isolation of the corresponding potassium adducts **1**⊃K^+. All have been fully characterized in solution and the solid-state using X-ray diffraction. In order to probe the interplay between the interactions associated with the potassium cation binding, the host−guest chemistry of **1** is contrasted with that of bis(imidazole-2-thione) **2** and calix[4]arene **3** (Figure 1). Density functional theory (DFT) calculations have also been used to help gain insight into the formation of these curious binuclear complexes.

Chart 1. Potassium Binding by Rhodium and Iridium-Based Hosts (COD = 1,5-Cyclooctadiene)



RESULTS AND DISCUSSION

Synthesis and Host−Guest Chemistry of Calix[4]-arenes 2 and 3. The new bis(imidazole-2-thione) ligand **2** was prepared through reaction of the corresponding bis-

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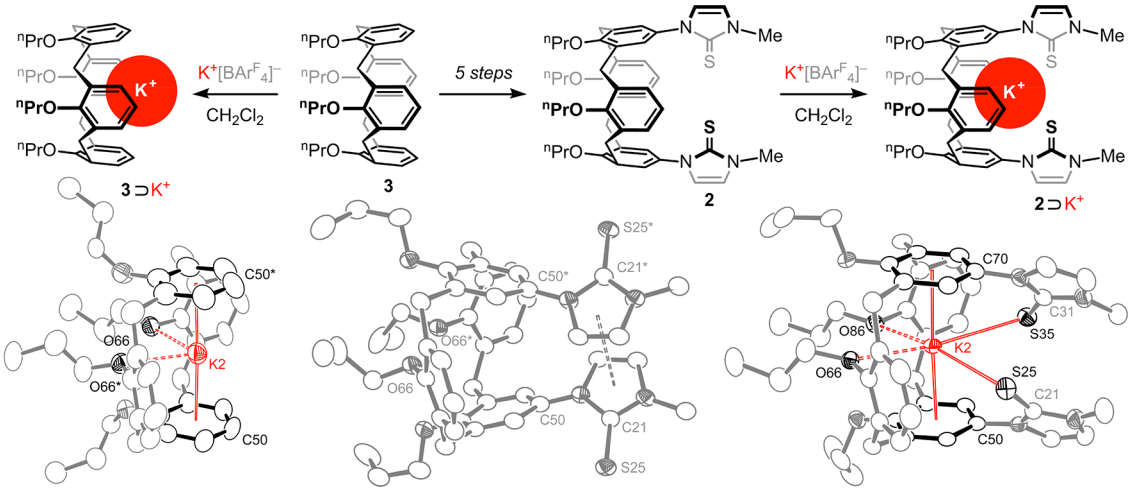

Figure 1. Potassium binding of **2** and **3**. Solid-state structures of **2**, **2**⊃K^+, and **3**⊃K^+ (ellipsoids drawn at 30%, 50%, and 30% probability, respectively; symmetry equivalent atoms indicated by asterisks; minor distorted components in **3**⊃K^+ omitted). $[BAr^F_4]^-$ counteranions omitted from all structures. Selected bond lengths (Å): **2**, S25−C21, 1.687(6); Cnt(N20−C24)−Cnt(N20*−C24*), 3.46(1); C50−C50*, 4.24(1) (* = x, 1 − y, $^1/_2$ − z); **2**⊃K^+, K2−S25, 3.4019(7); K2−S35, 3.4102(6); K2−Cnt(C50−55), 2.712(2); K2−Cnt(C70−75), 2.711(2); K2−O66, 2.845(1); K2−O86, 2.807(2); S25−C21, 1.679(2); S35−C31, 1.681(2); C50−C70, 5.306(3); **3**⊃K^+: K2−Cnt(C50−55), 2.790(9); K2−O66, 2.830(5); C50−C50*, 5.71(2) (* = 3 − x, $^3/_2$ − y, + z).

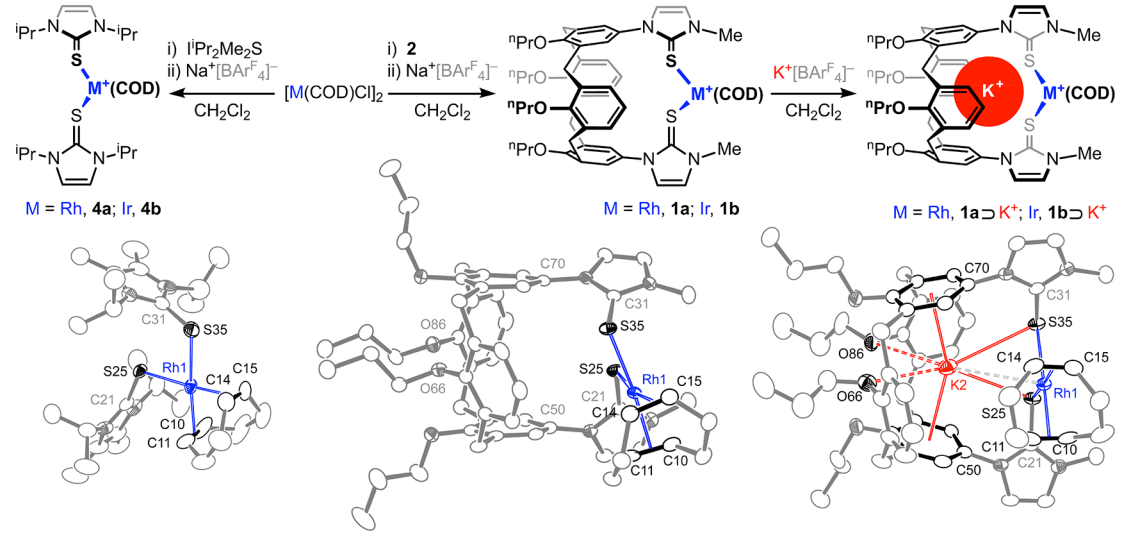

Figure 2. Preparation of **1**, **1**⊃K^+, and **4**. Solid-state structures of **1a**, **1a**⊃K^+, and **4a** (ellipsoids drawn at 50% probability; minor distorted components omitted). $[BAr^F_4]^-$ counteranions omitted from all structures. Selected bond lengths (Å) and angles (deg): **1a**, Rh1−Cnt(C10,11), 2.030(2); Rh1−Cnt(C14,15), 2.015(2); Rh1−S25, 2.3515(5); Rh1−S35, 2.3756(5); C10−C11, 1.386(3); C14−C15, 1.394(3); S25−C21, 1.705(2); S35−C31, 1.720(2); S25−Rh1−S35, 83.81(2); C50−C70, 5.387(3); **1b**, Ir1−Cnt(C10,11), 2.017(3); Ir1−Cnt(C14,15), 2.005(3); Ir1−S25, 2.3390(8); Ir1−S35, 2.3604(8); C10−C11, 1.407(5); C14−C15, 1.422(5); S25−C21, 1.709(3); S35−C31, 1.732(3); S25−Ir1−S35, 84.40(3); C50−C70, 5.385(5); **1a**⊃K^+, Rh1−K2, 3.715(1); Rh1−Cnt(C10,11), 2.023(4); Rh1−Cnt(C14,15), 2.029(4); Rh1−S25, 2.366(1); Rh1−S35, 2.3850(9); C10−C11, 1.387(7); C14−C15, 1.386(6); S25−C21, 1.716(4); S35−C31, 1.718(4); S25−Rh1−S35, 77.99(3); K2−S25, 3.472(1); K2−S35, 3.585(2); K2−Cnt(C50−55), 3.084(4); K2−Cnt(C70−75), 3.078(4); K2−O66, 3.149(3); K2−O86, 3.534(3); C50−C70, 6.709(5); **1b**⊃K^+, Ir1−K2, 3.690(1); Ir1−Cnt(C10,11), 2.015(5); Ir1−Cnt(C14,15), 2.016(5); Ir1−S25, 2.352(1); Ir1−S35, 2.364(1); C10−C11, 1.395(9); C14−C15, 1.381(8); S25−C21, 1.720(5); S35−C31, 1.729(5); S25−Ir1−S35, 78.80(4); K2−S25, 3.521(2); K2−S35, 3.632(2); K2−Cnt(C50−55), 3.068(5); K2−Cnt(C70−75), 3.065(5); K2−O66, 3.087(4); K2−O86, 3.514(4); C50−C70, 6.691(7); **4a**, Rh1−Cnt(C10,11), 2.010(3); Rh1−Cnt(C14,15), 2.020(3); Rh1−S25, 2.3706(6); Rh1−S35, 2.3671(7); C10−C11, 1.380(5); C14−C15, 1.380(5); S25−C21, 1.727(3); S35−C31, 1.729(3); S25−Rh1−S35, 89.06(2); **4b**, Ir1−Cnt(C10,11), 1.994(4); Ir1−Cnt(C14,15), 2.005(3); Ir1−S25, 2.3496(8); Ir1−S35, 2.3459(9); C10−C11, 1.396(6); C14−C15, 1.403(5); S25−C21, 1.728(3); S35−C31, 1.732(3); S25−Ir1−S35, 89.50(3).

(imidazolium) salt[4] with sulfur in the presence of weak base (72% isolated yield).[7] The solid-state structure of **2** is notable for π-stacking between the imidazole-2-thione moieties [Cnt−Cnt = 3.46(1) Å], which enforces a pronounced pinched cone conformation of the calix[4]arene scaffold and confers overall C_2 symmetry (Figure 1). Although retention of the π-stacking interaction is not apparent in CD_2Cl_2 solution at 298 K by ^{1}H NMR spectroscopy (600 MHz; C_{2v} symmetry), the onset of signal decoalescence was observed upon cooling to 200 K.

Mixing **2** with K[BAr^F_4] [Ar^F = 3,5-$(CF_3)_2C_6H_3$][8] in anhydrous CD_2Cl_2 resulted in dissolution of the otherwise insoluble salt and formation of the 1:1 host−guest complex **2**⊃K^+ (Figure 1). The system is under slow host−guest exchange on the NMR time scale (298 K, 400 MHz) and

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allowed the binding stoichiometry to be unambiguously verified through in situ experiments involving variation of the **2**/K[BAr^F_4] ratio (see Figure S44). On a preparative scale, the potassium adduct was isolated in high yield by crystallization (86%) and fully characterized. The solid-state structure of **2**⊃K^+ confirms encapsulation of the potassium cation within the calix[4]arene cavity (Figure 1). Supplemented by chelation of the thione (S−K^+ ca. 3.41 Å), the opposing aryl imidazole-2-thione units bind potassium [Cnt(Ar^S)−K^+ ca. 2.71 Å], in a sandwich-type π-complex arrangement. The adjacent aryl ether units are associated with $Ar^HO\cdots K^+$ contacts of ca. 2.83 Å. Sharp ^{1}H resonances and C_{2v} symmetry are observed for **2**⊃K^+ in CD_2Cl_2 across a wide temperature range (298−200 K, 600 MHz), indicating that the S−K^+ interaction is highly fluxional in nature.

In a similar manner, formation of a 1:1 potassium adduct of upper-rim-unfunctionalized calix[4]arene **3** was established in CD_2Cl_2 solution (slow host−guest exchange at 298 K, 400 MHz) and crystalline **3**⊃K^+ was subsequently obtained in 80% isolated yield. A core structure comparable to **2**⊃K^+ is observed in the solid state, exemplified by alternating arene−π interactions [2.790(9) Å] and short lower-rim oxygen contacts [2.830(5) Å] with the alkali-metal cation (Figure 1). In CD_2Cl_2 solution, potassium binding results in reduced structural dynamics of the otherwise flexible calix[4]arene scaffold on the ^{1}H NMR time scale (600 MHz): most notably, the slow exchange regime is reached at 200 K for **3**⊃K^+ (C_{2v}) but not for **3** (C_{4v}).

To help gauge the energetic importance of thione coordination in the formation of **2**⊃K^+, a competition experiment was carried out involving the reaction between **2** and **3**⊃K^+ in CD_2Cl_2 (eq 1). The resulting dynamic equilibrium showed selective binding of potassium by **2**, but the transfer of potassium from **3**⊃K^+ is only weakly exergonic ($\Delta G_{298\ K}$ = −8.4 kJ·mol^{-1}).[9] Together the combined solution data suggest that the potassium cation is primarily bound through the calix[4]arene scaffold in **2**⊃K^+, with comparatively weaker S−K^+ interactions. Consistent with this reasoning, 1,3-diisopropyl-4,5-dimethylimidazole-2-thione ($I^iPr_2Me_2S$)[10] does not form a potassium complex upon standing in a suspension of K[BAr^F_4] in CD_2Cl_2 at 298 K.[11]

$$\mathbf{2} + \mathbf{3}\supset K^+ \rightleftharpoons \mathbf{2}\supset K^+ + \mathbf{3} \qquad K_{298\ K} = 30 \pm 8 \qquad (1)$$

Reactions of **2**⊃K^+ and **3**⊃K^+ with 18-crown-6 resulted in quantitative extraction of potassium from both of the calix[4]arene hosts. Likewise, competition experiments involving [18-crown-6⊃K][BAr^F_4] [see the Supporting Information (SI) for preparation and solid-state structure; O−K^+ ca. 2.77 Å] and **2** or **3** showed no appreciable potassium uptake by the calix[4]arenes. Together these data indicate a relatively low absolute magnitude for the potassium cation binding by **2** and **3** and highlight the importance of employing weakly coordinating solvent and anion in the formation of **2**⊃K^+ and **3**⊃K^+.

Synthesis and Host−Guest Chemistry of Rhodium and Iridium Complexes 1. Cationic rhodium and iridium complexes [M(**2**)(COD)][BAr^F_4] (M = Rh, **1a**; M = Ir, **1b**) were prepared by reaction of $[M(COD)Cl]_2$[12] with **2** in CH_2Cl_2, followed by halide abstraction, and isolated in moderate yields (**1a**, 64%; **1b**, 68%; Figure 2). The formation of **1** were fully corroborated using a combination of NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), combustion analysis, and X-ray diffraction. Coordination of **2** is associated with a significant upfield shift of the C═S resonance (**1a**, δ 156.4; **1b**, δ 154.5; **2**, δ 163.4) and adoption of C_s symmetry in CD_2Cl_2 solution at 298 K (600 MHz). The solid-state structures show that the $\{M(COD)\}^+$ fragments are projected to one side of the calix[4]arene cavity through asymmetrical cis coordination of the imidazole-2-thione donors, one synperiplanar (S25) and the other antiperiplanar (S35) about the M−S vectors, conferring overall C_1 symmetry. Reconciling this structure in solution, gradual cooling from 298 to 200 K resulted in loss of C_s symmetry and signal decoalescence in the ^{1}H NMR spectra of **1** ($\Delta G^{\ddagger}$: ∼43 kJ·mol^{-1}, **1a**; ∼48 kJ·mol^{-1}, **1b**; Figures S4 and S9). Fluxional behavior of this type is well-known for complexes of sulfur-based ligands.[13] Bis(imidazole-2-thione) complexes [M($I^iPr_2Me_2S$)$_2$(COD)][BAr^F_4] (M = Rh, **4a**; Ir, **4b**; Figure 2)[14] were prepared for comparison and also adopt asymmetrical *cis*-thione geometries in the solid state but are significantly more structurally dynamic than **1** in solution.

The potassium binding of **1** was systematically investigated through in situ reactions involving varying ratios of K[BAr^F_4] in anhydrous CD_2Cl_2 (Figures S40 and S42). Partial uptake of potassium into solution and formation of 1:1 adducts **1**⊃K^+ (slow exchange at 298 K, 400 MHz) was observed (eqs 2 and 3). Association constants determined by integration of ^{1}H NMR data are consistent with marginally stronger potassium binding for **1a** (12 ± 2) compared to **1b** (8 ± 2). Analytically pure samples of **1**⊃K^+ were subsequently obtained in low yield by selective crystallization of the dications from solution (ca. 10%). Reestablishment of the equilibrium occurs upon dissolution of isolated **1**⊃K^+ in CD_2Cl_2 solution (ca. 24 h) but is sufficiently slow that the potassium adducts can be comprehensively characterized.

$$\mathbf{1a} + K^+(s) \rightleftharpoons \mathbf{1a}\supset K^+ \qquad K_{298\ K} = 12 \pm 2 \qquad (2)$$

$$\mathbf{1b} + K^+(s) \rightleftharpoons \mathbf{1b}\supset K^+ \qquad K_{298\ K} = 8 \pm 2 \qquad (3)$$

The solid-state structures of **1**⊃K^+ reveal the potassium cation bound within the calix[4]arene cavity in very close proximity to the transition-metal centers: $Rh^+\cdots K^+$ = 3.715(1) Å; $Ir^+\cdots K^+$ = 3.690(1) Å (Figure 2). Compared to **1**, the solid-state structures of **1**⊃K^+ are notable for more symmetrical, all-synperiplanar (about the M−S vectors) configurations of the thione donors. The associated C_s symmetry is also observed in CD_2Cl_2 solution at 298 K. This change in conformational preference was verified in silico (see the SI) and is presumably driven by electrostatic repulsion between the metal atoms. For instance, **1**⊃K^+ are characterized by significantly enlarged proximal Cnt(Ar^H)$\cdots M^+$ distances [M: Rh, 5.688(5) vs 4.869(2) Å; Ir, 5.705(7) vs 4.851(4) Å] and widened calix[4]arene cavity openings, as gauged through the (Ar^S)CN$\cdots$(Ar^S)CN separations [M: Rh, 6.709(5) vs 5.387(3) Å; Ir, 6.691(7) vs 5.385(5) Å], compared to **1**. Notably, the X-ray-derived metrics associated with the encapsulation of potassium by the calix[4]arene ligand in **1**⊃K^+ are indicative of a weaker interaction compared to those in **2**⊃K^+, viz. Cnt(Ar^S)−K^+ ca. 3.07 vs 2.71 Å, S−K^+ ca. 3.55 vs 3.41 Å, and $Ar^HO\cdots K^+$ ca. 3.12/3.52 vs 2.83 Å.

The partial uptake of potassium into solution observed for **1** and the solid-state metrics of **1**⊃K^+ both imply significantly weaker binding compared to **2**; observations supported by complete retention of potassium by **2** when **2**⊃K^+ was reacted with **1** in competition experiments (eq 4). The associated energetics ($\Delta G_{298\ K}$ ∼ +22 kJ·mol^{-1}) were instead assessed indirectly through competition experiments between **1** and

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$3\supset K^+$ in CD_2Cl_2 (eqs 5 and 6).[9] As for the association constants, the rhodium-based host appears to show a more pronounced capacity for potassium inclusion in these competition experiments [$(5 \pm 2$ vs $3 \pm 2) \times 10^{-3}$]; however, the large experimental error associated with these values prevents a definitive conclusion to be drawn. Given the weak nature of the S−K^+ interaction, it is rather unsurprising that no reactions were detected by ^{1}H NMR spectroscopy for control experiments involving **4** and either $K[BAr^F{}_4]$ (insoluble) or $3\supset K^+$ in CD_2Cl_2. Moreover, quantitative extraction of potassium from $1\supset K^+$ resulted upon addition of 18-crown-6. Thus, although **1** are competent hosts for potassium cation guests, this series of competition experiments unequivocally demonstrate the significant destabilizing effect of the $M^+\cdots K^+$ interaction.

$$\mathbf{1} + \mathbf{2}\supset K^+ \not\rightarrow \mathbf{1}\supset K^+ + \mathbf{2} \quad (4)$$

$$\mathbf{1a} + \mathbf{3}\supset K^+ \rightleftharpoons \mathbf{1a}\supset K^+ + \mathbf{3} \qquad K_{298\,K} = (5 \pm 2) \times 10^{-3} \quad (5)$$

$$\mathbf{1b} + \mathbf{3}\supset K^+ \rightleftharpoons \mathbf{1b}\supset K^+ + \mathbf{3} \qquad K_{298\,K} = (3 \pm 2) \times 10^{-3} \quad (6)$$

Computational Analysis of Potassium Binding. The interactions associated with formation of $1\supset K^+$ were analyzed computationally using a DFT-based energy decomposition analysis (EDA)[15] and compared to those of $2\supset K^+$ and $3\supset K^+$. Inspection of the deformation densities associated with fragmentation between K^+ and **1** reveals that the largest charge transfer occurs from the thione donors to potassium (illustrated for $\mathbf{1a}\supset K^+$ in Figure 3 and $\mathbf{1b}\supset K^+$ in Figure S65: $\Delta\rho_1$−$\Delta\rho_3$; E_ρ = −7.37 to −13.62 kJ·mol^{-1}). Interestingly, in $\Delta\rho_3$, some charge depletion is evident on the transition metal. Significant charge flow also occurs from the aryl ($\Delta\rho_4$−$\Delta\rho_6$; E_ρ = −5.41 to −7.67 kJ·mol^{-1}) units of the calix[4]arene to potassium but curiously not from the lower-rim oxygen atoms (E_ρ < 5 kJ·mol^{-1}), suggesting that the short $Ar^H O\cdots K^+$ contacts of ca. 3.12/3.52 may result from the pinched cone conformation of the calix[4]arene scaffold rather than any meaningful bonding. Equivalent arene−π (E_ρ = −4.81 to −9.92 kJ·mol^{-1}) and thione (E_ρ = −15.78 to −17.07 kJ·mol^{-1}) interactions with the potassium cation can be identified in $2\supset K^+$, with the larger magnitude of these interactions consistent with weaker bonding in $1\supset K^+$ (Figure S66). Even stronger potassium bonding with the aryl units of **3** (E_ρ = −7.01 to −12.73 kJ·mol^{-1}) is evident in $3\supset K^+$ and supplemented in this case by a small degree of charge transfer from the lower-rim oxygen atoms to potassium (Figure S67).

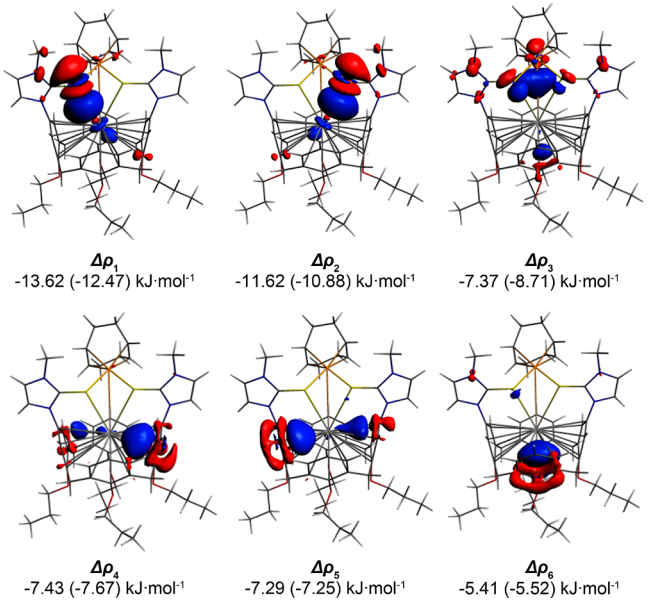

Figure 3. Leading ETS-NOCV deformation densities ($\Delta\rho$) and associated eigenvalues for fragmentation between K^+ and **1a** in $\mathbf{1a}\supset K^+$. Charge flow from red to blue. Energies associated with the equivalent deformation densities in $\mathbf{1b}\supset K^+$ are given in parentheses.

The total bonding energy values derived from EDA (E_{Int}) corroborate the relative potassium binding strengths established experimentally (**2** > **3** ≫ **1a** > **1b**; Table 1). The similarity of the orbital interaction energies for all of the host−guest adducts (ca. −126 kJ·mol^{-1}) suggests that this bonding component is associated almost exclusively with the calix[4]arene scaffold and marks out electrostatic interactions as the origin of the differences in the binding energy. Correspondingly, it is evident from these data that the ability of **1** to bind potassium, albeit weakly, is only possible because the electrostatic repulsion between potassium and the transition-metal cations (ca. +266 kJ·mol^{-1}) is *partially* offset by the electrostatic attraction between potassium and the thione donors (ca. −64 kJ·mol^{-1}), and there are significant orbital interactions between the potassium cation and the calix[4]arene cavity. Hirshfeld charges for **1** highlight greater charge differences between the sulfur and rhodium (−0.12/+0.19) than between the sulfur and iridium (−0.09/+0.07), which presumably accounts for the slightly less unfavorable electrostatic term in the EDA of $\mathbf{1a}\supset K^+$, compared to $\mathbf{1b}\supset K^+$, and correspondingly the marginally different binding affinities of the transition-metal-based hosts.

Table 1. EDA of Host−Guest Complexes of Potassium (Energies in kJ·mol^{-1})

host	E_{Pauli}	$E_{Electro}$	$E_{Orb\ Int}$	E_{Int}
1a	58.46	46.65	−125.37	−20.26
1b	56.09	54.00	−125.41	−15.32
2	78.00	−215.79	−122.70	−260.50
3	91.04	−151.76	−128.93	−189.65

SUMMARY AND OUTLOOK

The preparation and host−guest chemistry of cationic rhodium and iridium complexes (**1**) of a new bis(imidazole-2-thione)-functionalized calix[4]arene ligand (**2**) have been presented. Contrary to significantly destabilizing Coulombic repulsion resulting from close proximity to the bound transition metal, these complexes are competent hosts for the 1:1 binding of potassium cations within the central ligand cavity. The formation and constituent bonding of the resulting hetero-bimetallic adducts ($1\supset K^+$) has been interrogated through extensive solution and solid-state characterization, examination of the host−guest chemistry of **2** and its upper-rim-unfunctionalized calix[4]arene analogue **3**, and use of DFT-based EDA. On the basis of this work, the formation of $1\supset K^+$ can be attributed to robust potassium binding by the calix[4]arene scaffold and the ability of the thione donors to partially offset the destabilizing electrostatic repulsion associated with close proximity of the two metal centers ($M^+\cdots K^+$ = 3.7 Å, where M = Rh, Ir).

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In the context of host−guest chemistry, the formation of **1**⊃K^+ showcases an unusual confluence of bonding interactions that may inform new approaches for engineering effective molecular receptors, while from an organometallic chemistry perspective, the use of a cavitand-based ligand, such as **2**, to study the unusual coordination chemistry of the late transition metals is a potentially powerful concept. We are particularly interested in exploring the latter as part of our ongoing research at the interface of supramolecular and organometallic chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02441.

Full experimental and computational details, NMR and ESI-MS spectra of new compounds, and selected reactions (PDF)

Optimized geometries in .xyz format (XYZ)

Accession Codes

CCDC 1569667−1569677 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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